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## 6. AUTHOR(S)

J.A. Harrison, C.T. White, R.J. Colton,  
and D.W. Brenner

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Molecular dynamics simulations have been used to model the dynamics of indentation and the resulting damage for a (111) surface of a (1x1) hydrogen terminated diamond tip interacting with the (111) surface of both a (1x1) hydrogen terminated diamond crystal and a non-hydrogen terminated diamond crystal. In both cases, indentation can result in a non-adhesive (i.e. elastic) or an adhesive (i.e. plastic) interaction depending on the maximum value of the applied load. Further, adhesion is usually accompanied by fracture and is independent of where the tip contacts the surface. In the case of the hydrogen terminated crystal, the diamond crystal structure is significantly disrupted as a result of the indentation. When the hydrogen is removed from the crystal's surface, adhesion occurs at lower loads than previously observed. However, the crystal structure is not significantly altered as a result of the indentation. The state of the surface dictates the type of indentation mechanism.

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J.A. Harrison, C.T. White, R.J. Colton, and D.W. Brenner

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Nanoscale Investigation of Indentation, Adhesion  
and Fracture of Diamond (111) Surfaces

† J.A. Harrison, C.T. White, R.J. Colton, and D.W. Brenner

Chemistry Division, Code 6170  
Naval Research Laboratory  
Washington, D.C. 20375-5000, U.S.A.

ABSTRACT

Molecular dynamics simulations have been used to model the dynamics of indentation and the resulting damage for a (111) surface of a (1 x 1) hydrogen terminated diamond tip interacting with the (111) surface of both a (1 x 1) hydrogen terminated diamond crystal and a non-hydrogen terminated diamond crystal. In both cases, indentation can result in a non-adhesive (i.e. elastic) or an adhesive (i.e. plastic) interaction depending on the maximum value of the applied load. Further, adhesion is usually accompanied by fracture and is independent of where the tip contacts the surface. In the case of the hydrogen terminated crystal, the diamond crystal structure is significantly disrupted as a result of the indentation. When the hydrogen is removed from the crystal's surface, adhesion occurs at lower loads than previously observed. However, the crystal structure is not significantly altered as a result of the indentation. The state of the surface dictates the type of indentation mechanism.

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† Author to whom correspondence should be addressed

## 1. Introduction

Diamond is the hardest known material and is highly resistant to plastic deformation. Traditionally, the adhesion and hardness of diamond have been examined on the macroscopic scale. The hardness of diamond depends on various parameters, e.g. crystallographic face and indenter size [1]. For example, Young's Moduli for the (111) and the (100) faces of diamond are 1274 and 1179 GPa, respectively [2]. The adhesion of diamond is thought to depend on bulk properties as well as surface properties [3]. Recent technological advances have begun to make the experimental and theoretical investigation of these properties on the nanoscale feasible. In addition to the imaging of ordered surfaces of crystalline materials [4,5] and the imaging of overlayers [6,7]; a few groups have used the atomic force microscope (AFM) to investigate the mechanical properties of surfaces [8] and thin films [9,10]. In addition, Mate and coworkers [11,12] have studied the atomic scale mechanism of friction, as friction is thought to have an adhesive component [3]. Molecular dynamics (MD) simulations [13,14] have been previously used to investigate the atomistic mechanism of adhesion, indentation, and fracture of metals in contact.

Molecular dynamics was used earlier to investigate the interactions which arise when two diamond slabs are brought into contact [15]. These simulations demonstrated that the chemical nature and the geometry of the slab-slab interface have an effect on the ultimate outcome of the interaction (i.e. adhesion versus non-adhesion). In this work, molecular dynamics simulations of a diamond tip indenting a diamond crystal have been undertaken in an effort to understand the mechanisms of indentation and adhesion on the atomic scale. These are the first reported calculations of this type with a tip-crystal geometry for diamond systems.

## 2. Methodology

The molecular dynamics calculations were carried out by integrating Newton's equations of motion with a third order variable time step Nordsieck predictor corrector [16]. The forces are derived from an empirical hydrocarbon potential that is capable of modeling intramolecular chemical bonding in both diamond and graphite lattices, as well as in a variety of small hydrocarbon molecules [15,17,18]. The potential used here is potential II of reference 17 with additional terms that better describe torsional forces and short range repulsive terms which may prove important under high compression. Unlike more traditional valence-force fields, this potential allows for bond breaking and forming along with associated changes in atomic hybridization, thus modeling chemical reactivity. We note, however that because an explicit treatment of electrons is replaced with a many-body classical expression, forces arising from effects such as orbital resonance and symmetry may not necessarily be realistically treated. Also, since we are interested in adhesion that arises from the formation of covalent bonds, we have neglected any long range forces that may arise from van der Waals or related interactions. Recently, this potential has been used to model the compression of  $C_{60}$  between graphite planes [18], the scattering of  $C_{60}$  from diamond surfaces [19], and the compression mechanism in the [111] direction of diamond crystals [15].

In this work, the (111) face of a (1 x 1) hydrogen terminated diamond tip is used to indent the (111) surface of a (1 x 1) hydrogen terminated diamond crystal and the (111) surface of a non-hydrogen terminated diamond crystal. The diamond (111) surface consists of first and second layer carbon atoms which are trigonally arranged. The vertices of these triangles are rotated 60 degrees with respect to one another, thus forming a hexagon. (It is important to note that this hexagon is not planar but rather more similar to the chair conformation in cyclohexane.) These hexagons are centered over the fourth

layer carbon atoms, which are visible through "holes" in the surface layer. The normal bulk spacing is 0.515 Å between first and second layer atoms, 1.546 Å between second and third layer atoms, and 0.515 Å between third and fourth layer atoms [20]. The first layer atoms are hydrogen terminated. Removing the hydrogen atoms leaves radical sites causing relaxation in the first and second layers of the surface. The potential predicts that carbon-carbon bonds between first and second layers contract by 3.5 % and those between the second and third layers expand by 1.9 % relative to bulk values. These values are in good agreement with those obtained from first principle calculations (-3.1 % and 2.1 %, respectively) [21]. Although this potential correctly predicts the (2 x 1) reconstructed surface to be lower in energy than the (1 x 1) surface with the radical sites [19], on the time scale of these simulations no reconstruction was observed.

Although this potential does very well predicting atomics spacings and energetics for diamond lattices, it does less well predicting the elastic constants of diamond [22]. Further, classical elasticity theory states that Young's modulus for the indentation of the (111) face of a cubic material is related to the elastic constants,  $c_{ij}$ , via the following relationship

$$E(111) = 6c_{44}(c_{11} + 2c_{12})/(c_{11} + 2c_{12} + 4c_{44}). \quad (1)$$

The potential used here yields a value of 1364 GPa [22] for  $E(111)$  compared to the experimentally determined value of 1274 GPa [2]. AFM experiments are currently in progress which will allow for the direct comparison of MD results, experimental data, and classical elasticity theory.

The tip and the crystal both contain 10 layers of carbon atoms and two layers of hydrogen atoms. In the crystal, each layer contains 64 atoms. Periodic boundary conditions are applied in the x-y plane which contains the (111) surface of the crystal. This simulates an infinite (111) surface for indentation

with the tip. The tip was constructed by removing atoms from a (111) crystal (which was similar to the surface) until it looked approximately like an inverted pyramid with a flattened apex (see Fig. 1). Hydrogen atoms were added to the edge carbon atoms, i.e. the sides of the tip, to satisfy the valency requirements of the carbon atoms (the tip contained a total of 325 atoms). Because the tip-crystal system is not infinite in the direction perpendicular to the (111) surface, the outer most layers of the tip and the surface are also terminated with hydrogen. Figure 1 shows the starting configurations for the tip-crystal systems examined here. The two outer most layers (z direction) of the tip and the crystal were both held rigid. Moving toward the center of the tip and the crystal from the rigid layers; frictional forces [23] are applied to the next 6 layers within the tip and the crystal to control the temperature of the system during the simulations. The 4 innermost layers of both the tip and the crystal have no constraints. These simulations are carried out at 300 Kelvin.

Indentation is performed in the following way. The rigid layers of the tip are moved toward the crystal in steps of  $0.15 \text{ \AA}$ . The tip-crystal system is then allowed to equilibrate for 250-500 time steps of the order 0.1 femtoseconds. Once the system equilibrates, the applied load on the tip in the [111] (or z) direction is calculated by summing the forces on all the tip atoms in this direction. This number is then averaged over the next 125-250 time steps. The rigid layer of the tip is then moved another  $0.15 \text{ \AA}$  closer to the surface and the above process is repeated. Retraction of the tip involves the reverse of the process described above, i.e. movement of the rigid layers of the tip away from the crystal followed by equilibration. Although these indentation rates are orders of magnitude faster than typical experimental values, they are sufficiently slow to allow equilibration of the system. For example, the overall indentation rate of approximately  $0.30 \text{ km/sec}$  is much slower than the speed of sound in diamond (12 to  $18 \text{ km/sec}$  depending on propagation direction

[24]). This allows the thermostat to dissipate any reflected waves that arise from motion of the tip.

Throughout the course of the simulation the following quantities are monitored: 1) the total potential energy of the system; 2) the applied load on the tip; and 3) the average vertical position of all the layers in the crystal and in the tip. The vertical position of any given layer is defined as the average vertical position ( $z$  position) of all the atoms contained in that layer. The quantity  $z_{rd}$  is defined as the vertical distance between the outermost rigid layers of the tip and the crystal (see Fig. 1). The approximate distance between tip and the surface can be obtained by subtracting the sum of the tip and crystal vertical heights at time zero from  $z_{rd}$ . The sum of the initial tip and crystal vertical positions for the hydrogen terminated surface system and the non-hydrogen terminated surface system are 21.9 and 20.7 Å, respectively.

### 3. Results

To determine if adhesion is load dependent, indentations of both a hydrogen terminated diamond (111) surface and a non-hydrogen terminated diamond (111) surface were carried out for two different values of maximum applied load (200 nN and 250 nN). In these simulations the applied load is increased by decreasing the distance between the rigid layers of the tip and the rigid layers of the surface. For a given simulation, the reported maximum applied load is defined as the value of applied load on the tip before retraction of the tip from the surface.

#### A. Hydrogen Terminated Diamond (111)

For the 200 nN indentation, the potential energy as a function of  $z_{rd}$  for the hydrogen terminated diamond (111) surface is shown in Fig. 2a. These data show no significant hysteresis, which is indicative of a non-adhesive or elastic interaction. Further evidence for this conclusion can be derived from an



analysis of the atomic positions at various points in the simulation (Fig. 3a-d). It is apparent from a comparison of the initial and final tip-crystal geometries that the system has undergone an elastic interaction.

Increasing the applied load on the tip to 250 nN leads to different behavior. In this case, the tip and the surface yield plastically resulting in adhesion between the tip and the crystal. This is apparent from an analysis of the potential energy versus  $z_{rd}$  data (Fig. 2b), which show significant hysteresis, and from examination of the atomic positions throughout the simulation (Fig. 3e-h), which clearly show bond formation between the tip and the crystal. As the tip is pulled back from the crystal connective strings of atoms are formed. As the distance between the tip and crystal increases these strings break one by one. Each break is accompanied by a sudden drop in the potential energy at large positive values of  $z_{rd}$  (see Fig. 2b). This process continues until all the connections are severed. (It is worth noting that for all cases examined here plots of applied load versus  $z_{rd}$  show similar trends and are therefore not shown.)

A "microscopic" value of hardness can be estimated from these data. For the (111) face of diamond it is approximately 1200 GPa. This value is an order of magnitude larger than the typical bulk hardness (100 GPa) [1], however for small contact areas the apparent hardness has been shown to rise above the bulk value [25]. Thus, it may be more appropriate to compare the hardness values obtained with the MD simulation with those obtained with an AFM. (We have recently compared the MD simulated indentation curves for diamond (111) and (100) and graphite with AFM measured curves for diamond (100) and graphite [22]. While the results do not agree quantitatively (and differ substantially from bulk values), the correct trend in hardness is observed, i.e. diamond (111) > diamond (100) >> graphite.)

Owing to the nature of molecular dynamics simulations, the mechanism of the indentation can be examined on the nanoscale. Figure 4a-b shows the

initial stages of indentation looking at the surface (through the tip) along the [111] direction. In this simulation, the hydrogen terminated carbon atoms of the tip are positioned over the second layer carbon atoms of the surface. Similarly, the second layer carbon atoms of the tip are positioned over the hydrogen terminated carbon atoms on the surface. Although the diamond lattice of the tip is not in registry with the diamond lattice of the surface, this is a symmetric loading situation because the tip atoms are lined up directly over surface atoms and not over bonds. In other words, the holes in the tip are lined up with the holes in the surface. For clarity, only tip atoms in those layers that are closest to the crystal surface are shown in Fig. 4. From an analysis of the indentation sequence shown in Fig. 4a-b it is apparent that as the tip and the crystal begin to interact, the carbon atoms along the periphery of the tip move slightly to one side in an effort to minimize the carbon-hydrogen repulsion. However, the center atoms of the tip remain approximately stationary. This results in a *twisting* type of motion for the tip in the early stages of indentation. After this initial twisting the tip settles into its minimum energy configuration for indentation. The twisting causes atoms in the tip and crystal to be out of alignment (Fig. 4b). That is, most carbon atoms of the tip are no longer lined up directly over surface carbon atoms, but over bonds. This situation can be thought of as *asymmetric* loading. Ultimately, asymmetry during indentation results in damage to the periodic (111) structure of the original crystal (Fig. 4c) owing to the bond formation between tip atoms and subsurface carbon atoms.

After indentation and subsequent separation, there is a transfer of carbon species from the tip to the surface and vice versa. Further, it is possible to transfer hydrogen atoms from the tip to a subsurface carbon atom of the diamond crystal (Fig. 4c).

#### B. Non-Hydrogen Terminated Diamond (111)

For the 250 nN indentation of the (111) surface of a non-hydrogen terminated diamond crystal, the potential energy as a function of  $z_{Td}$  is shown in

Fig. 2c and the atomic positions at various times during the simulation are shown in Fig. 5. Both sets of data indicate that the tip-crystal system has undergone an adhesive interaction. In contrast to the indentation of a hydrogen terminated diamond (111) surface, when hydrogen is removed from the surface adhesion can be achieved when the applied load is 200 nN.

There are several notable differences in this case as compared to the indentation of the hydrogen terminated diamond crystal discussed above. For example, the mechanism of indentation differs. As the tip and the surface layer of the crystal begin to interact, the entire tip (except for the rigid layer) slides by half a lattice spacing such that the hydrogen atoms on the tip fall into the holes on the surface of the crystal and the atoms which contain the radical sites on the surface align with the lattice holes of the tip. This arrangement places the second layer carbon atoms of the tip and crystal directly over the top of one another resulting in a *symmetrically* applied load during indentation. This is demonstrated in the indentation sequence shown in Fig. 4d-e, where the initial tip-crystal alignment was such that the hydrogen terminated tip atoms were again placed above the second layer carbon atoms of the crystal. As a result of this differing indentation mechanism the indentation itself appears to be more ordered (Fig. 5a-d) than previously observed. Moreover, examination of the interface between the tip and the surface reveals that the adhesive (new) bonds which have been formed are formed exclusively between the tip and the undercoordinated surface carbon atoms. As the tip is pulled back from the surface, the tip-crystal system tends to elongate until the point of fracture is reached. This fracture does not appear to occur in discrete steps as in the previously discussed example, but rather it occurs in a more concerted fashion. This is demonstrated in the qualitatively different shape of the potential energy versus distance curves shown in Figs. 2b and 2c. In this case, the potential energy increases to a maximum value at  $z_{rd} \approx 25 \text{ \AA}$  followed by a smooth decrease at larger values of  $z_{rd}$ .

Finally, when the indentation and retraction are complete both carbon species and hydrogen have been transferred from the tip to the surface only. Additionally, the crystal sustains no significant damage to its (111) structure as a result of the symmetrically applied load during the indentation compared to the case of the hydrogen terminated diamond crystal. This is apparent from an analysis of Fig. 4f.

#### 4. Discussion

Several observations can be made about the nature of the adhesive interaction. First, adhesion during indentation is dependent upon the maximum value of applied load. At low values of applied load the interaction is non-adhesive, whereas at higher values of applied load the interaction is adhesive. The non-adhesive interaction is not too surprising since diamond is fairly chemically inert. Additionally, previous MD simulations have shown that when two diamond (111) slabs are pushed together, the surfaces will not adhere when both (or just one) of the surfaces are hydrogen terminated [15]. The present simulation predicts that breaking the symmetry of the system facilitates adhesion. (In the case where two diamond slabs are interacting, asymmetry is achieved when hydrogen atoms are randomly removed from both surfaces.) The tip-crystal system examined here, however, has no such inherent geometric symmetry. Increasing the applied load on the tip increases the contact pressure causing the surface to yield plastically facilitating adhesion between the tip and the surface.

Second, when the hydrogen is removed from the surface of the diamond crystal, adhesive behavior is observed for smaller values of applied load. This can be attributed to the increased surface energy of the diamond crystal when the hydrogen is removed [3]. This phenomenon is also observed in experimental investigations of surface forces using the AFM [9]. In these studies increasing

the surface energy increases the pulloff force required to separate the tip-substrate system. Experiments between crossed cylinders of diamond [26] (in vacuum) showed that the adhesion was surprisingly small (about 1000 times smaller than expected based on surface energy calculations). However, the exact nature and composition of the surface and its corresponding roughness were not indicated and therefore no firm conclusion can be drawn from these observations.

Third, adhesion is always accompanied by fracture. The adhesive interaction observed here is a bonding interaction unlike other types of adhesive interactions such as capillary interactions or molecule entanglement which are sometimes observed experimentally [27]. Once these bonds have been formed, fracture usually occurs in the tip due to its decreased strength as compared to the semi-infinite surface. However, it is also possible to transfer surface atoms to the tip. Experimentally adhesion can lead to fracture of the diamond surfaces. For example, the high friction and the associated wear of the diamond surfaces in vacuum is believed to be due to the adhesion of the diamond surfaces [28].

Finally, these simulations have been repeated with the tip and crystal aligned differently at the start of the indentation. The above conclusions regarding non-adhesive and adhesive interactions are unchanged. That is, adhesion is dependent on the maximum value of applied load achieved and not on the geometry of the initial contact. Furthermore, the conclusions regarding the *twist* and *shift* mechanisms remain unchanged. That is, when a hydrogen terminated tip indents a hydrogen terminated crystal the tip atoms may twist in the early stages of indentation to minimize repulsive interactions. When the surface is not hydrogen terminated the entire interacting portion of the tip may shift to an adjacent lattice position.

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## Figure Captions

Figure 1. Starting tip-crystal configurations for the systems investigated. These systems are: A) a hydrogen terminated diamond (111) tip and a hydrogen terminated diamond (111) crystal separated by 1.8 Å ( $z_{rd} = 23.7$  Å); and B) a hydrogen terminated diamond (111) tip and a non-hydrogen terminated diamond (111) crystal separated by 2.5 Å ( $z_{rd} = 23.1$  Å). Periodic boundary conditions are imposed in the x-y plane.

Figure 2. Total potential energy of the system as a function of rigid layer separation for compression and expansion. Panels A and B show these data when both the tip and the surface are hydrogen terminated. The maximum value of applied load in A) is 200 nN and 250 nN in B). Panel C shows these data for the hydrogen terminated tip interacting with a non-hydrogen terminated surface. The maximum value of applied load is 250 nN in C). Arrows indicate the direction of the motion.

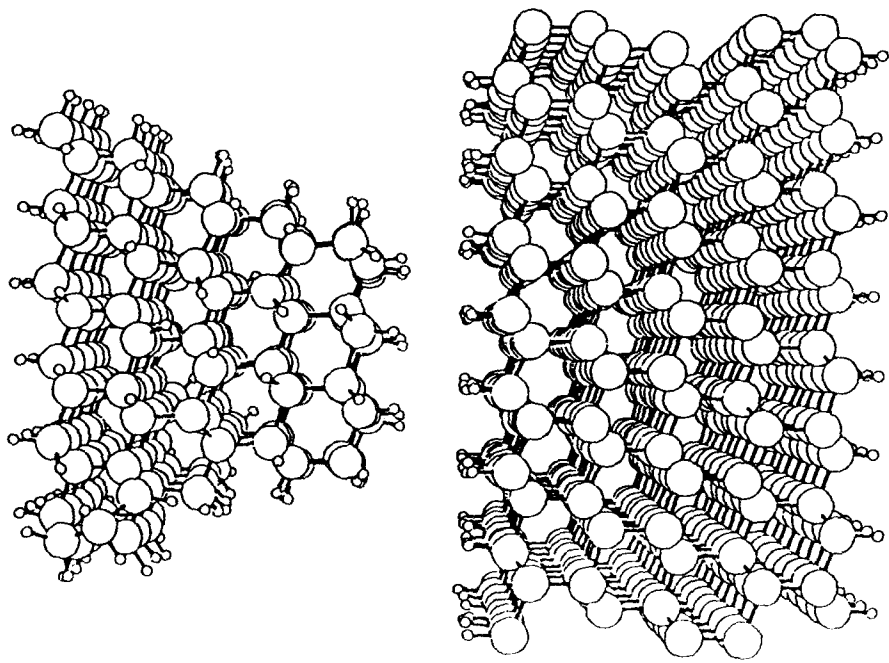
Figure 3. Atomic positions at various times during the *non-adhesive* indentation of the hydrogen terminated (111) diamond surface with a hydrogen terminated diamond (111) tip. The rigid layer separations ( $z_{rd}$ ) are: A) 20.5 Å (1.6 ps), B) 17.8 Å (2.9 ps), C) 21.1 Å (3.7 ps), and D) 23.8 Å (4.4 ps). Atomic positions at various times during the *adhesive* indentation of the hydrogen terminated (111) diamond surface with a hydrogen terminated diamond (111) tip. The rigid layer separations are: E) 20.7 Å (1.6 ps), F) 16.3 Å (3.5 ps), G) 26.5 Å (8.6 ps), and H) 31.0 Å (10.9 ps).

Figure 4. Atomic positions during the initial stages of indentation looking at the surface (through the tip) along the [111] direction for a hydrogen terminated diamond (111) tip indenting a *hydrogen* terminated (111) crystal (panels A and B). The rigid layer separations are: A) 21.1 Å (1.3 ps) and B) 20.1 Å (1.8 ps). Final atomic positions after indentation and retraction for this same tip-crystal system are shown in panel C ( $z_{rd}=31.0$  Å (10.9 ps)). (In this case

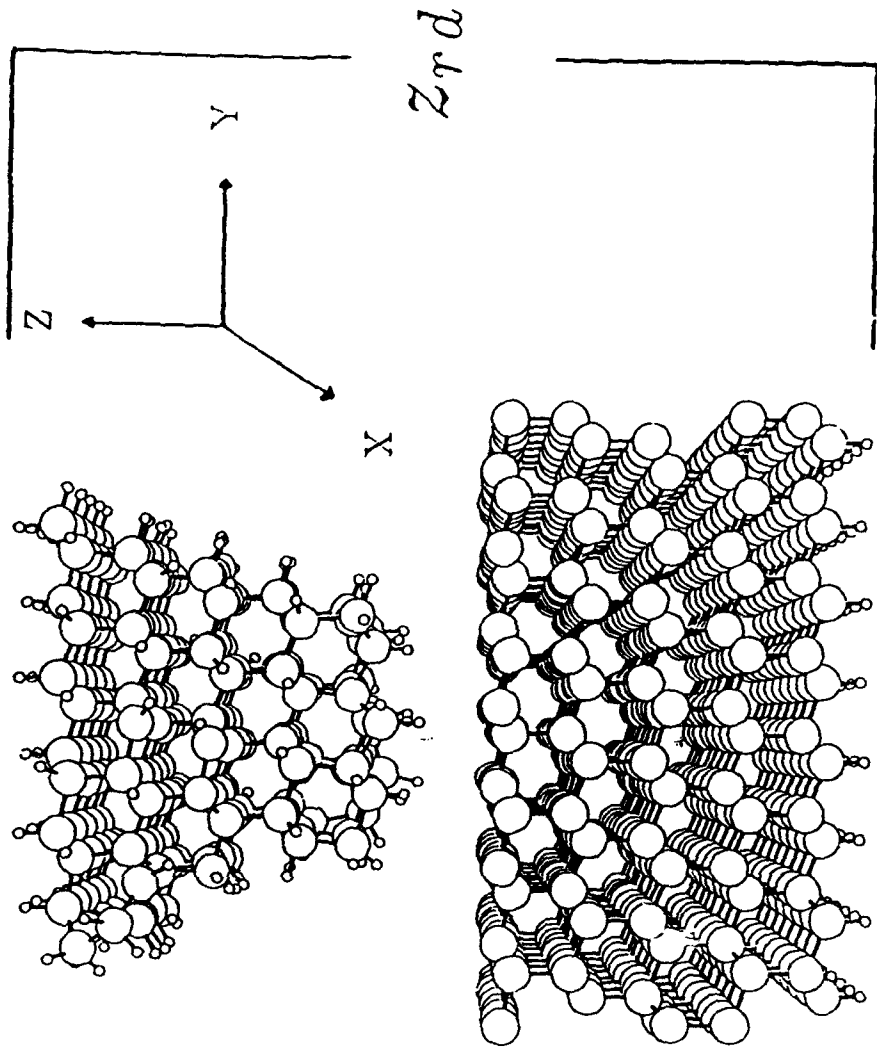
the crystal sustains significant damage to its (111) structure.) Atomic positions during the initial stages of indentation viewed from the [111] direction as above for a hydrogen terminated diamond (111) tip indenting a *non-hydrogen* terminated (111) crystal (panels D and E). The rigid layer separations are: D) 22.5 Å (0.18 ps) and E) 20.3 Å (0.73 ps). Final atomic positions after indentation and retraction are for this same tip-crystal system are shown in panel F ( $z_{rd}=32.4$  Å (10.9 ps)). In panels A, B, D, and E cross hatched atoms are the hydrogen containing carbons on the tip and solid atoms are second layer carbon atoms of the tip. In panels C and F, cross hatched atoms are carbon atoms that originated from the tip, solid atoms are hydrogen atoms which originated from the tip. The cross-hairs have been added for reference.

Figure 5. Atomic positions at various times during the *adhesive* indentation of the hydrogen terminated (111) diamond surface with a non-hydrogen terminated diamond (111) tip. The rigid layer separations are: A) 20.9 Å (0.58 ps), B) 16.5 Å (1.6 ps), C) 25.8 Å (2.7 ps), and D) 32.4 Å (3.5 ps).

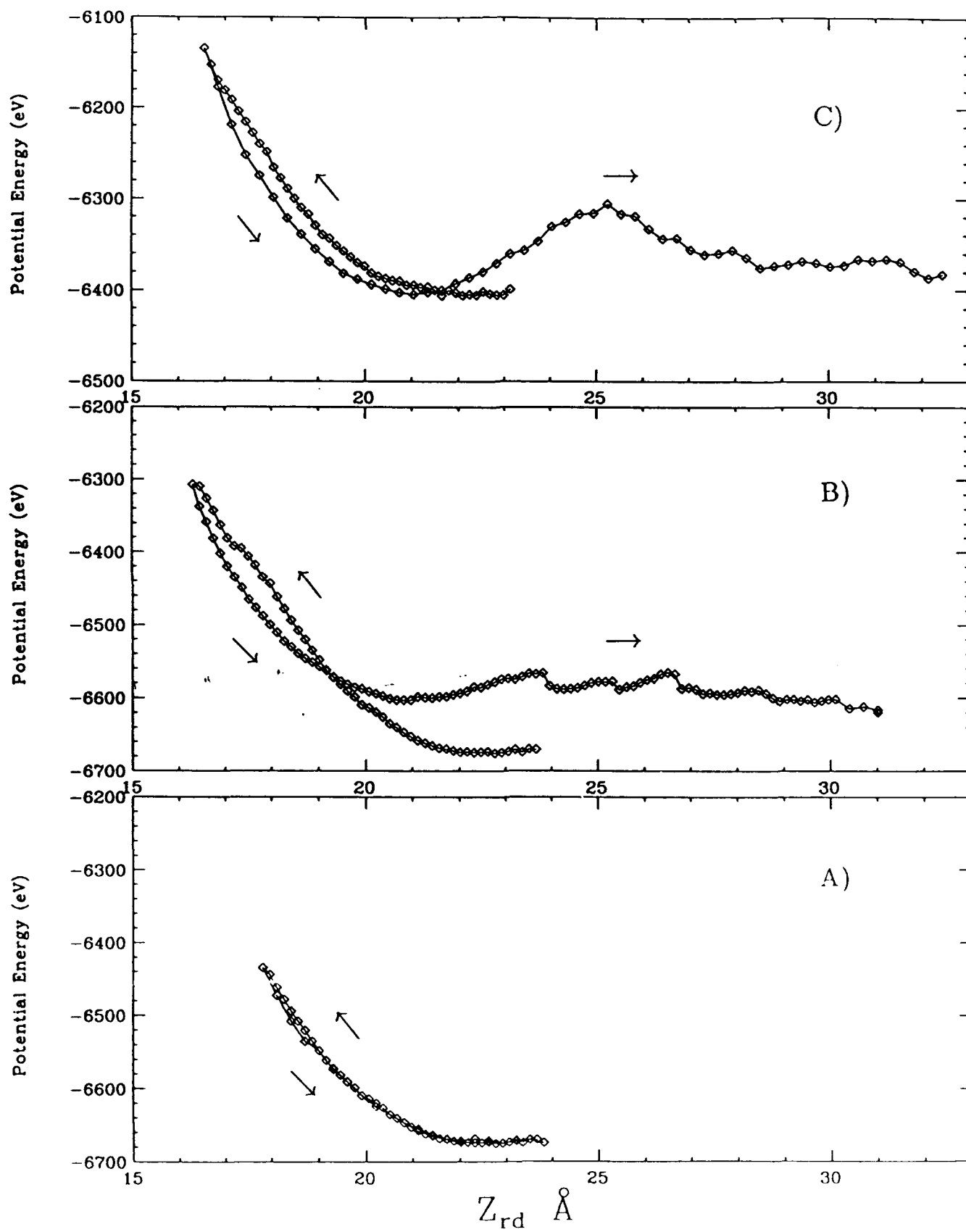
A)

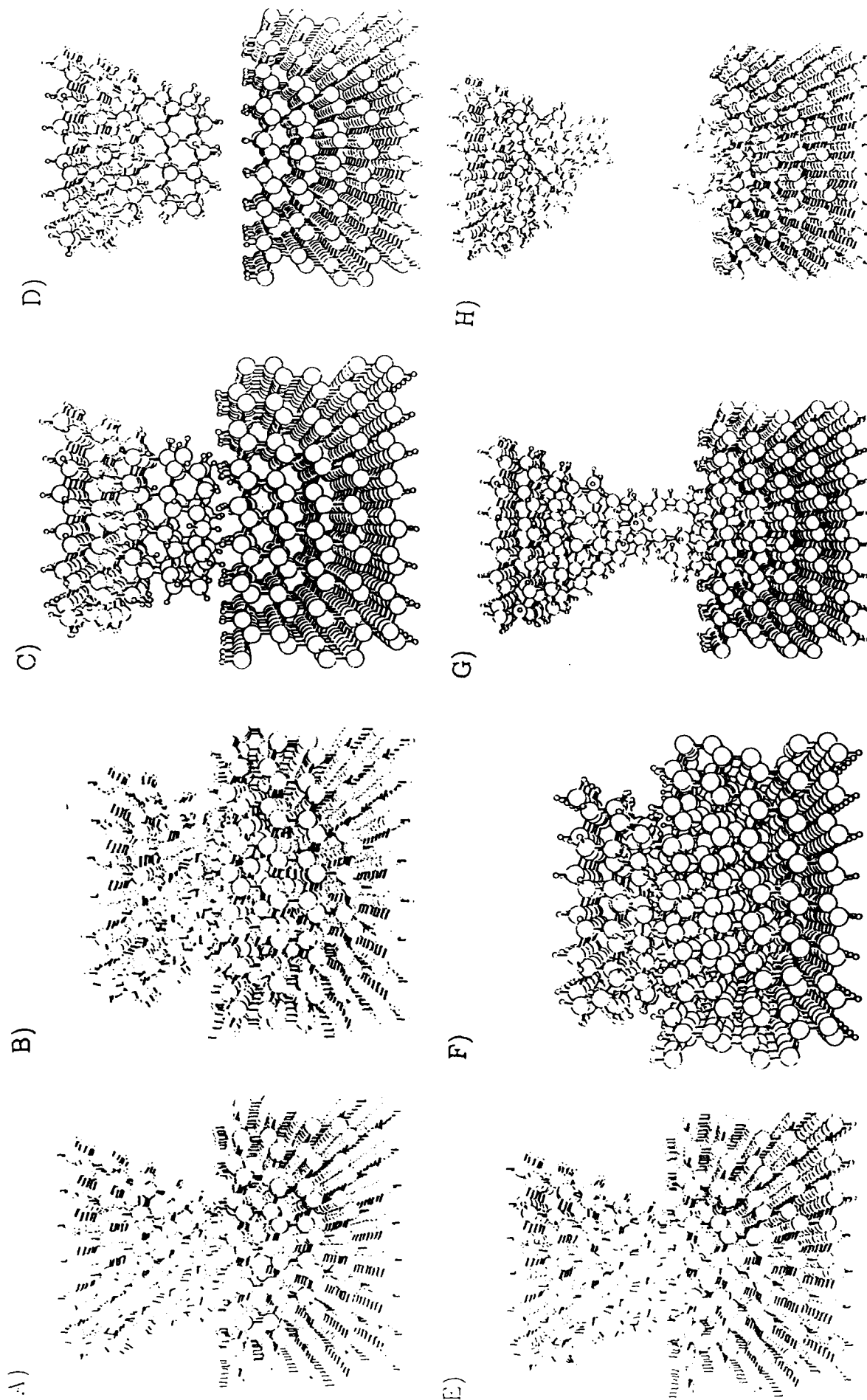


B)

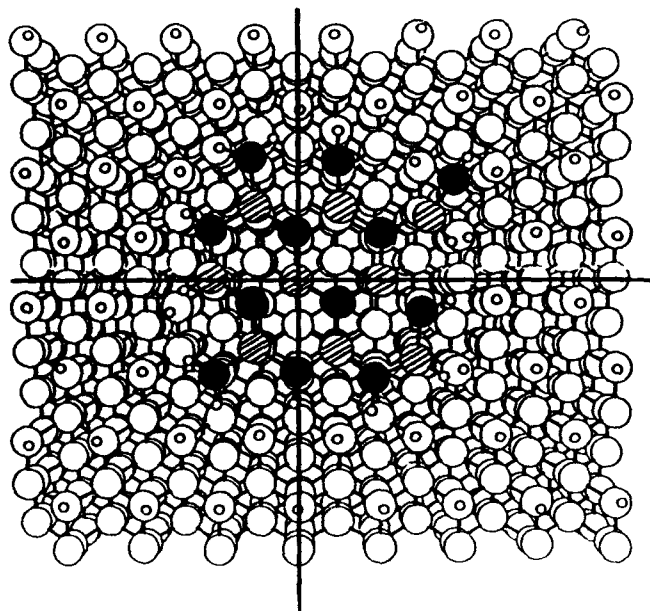


# Potential Energy vs. Distance

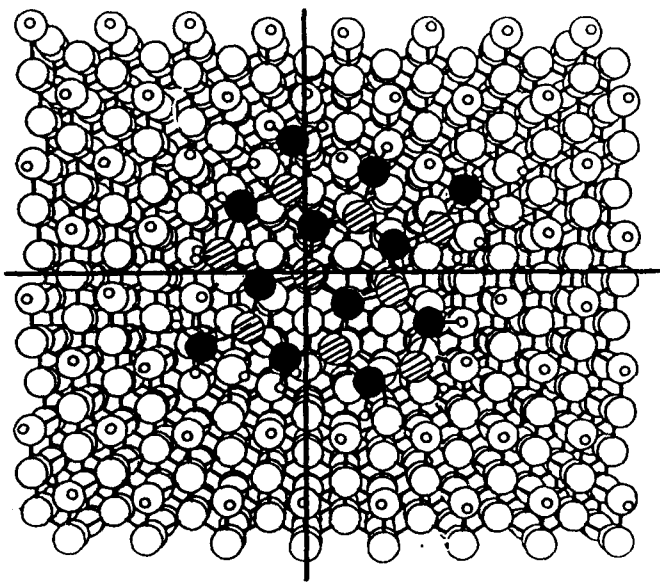




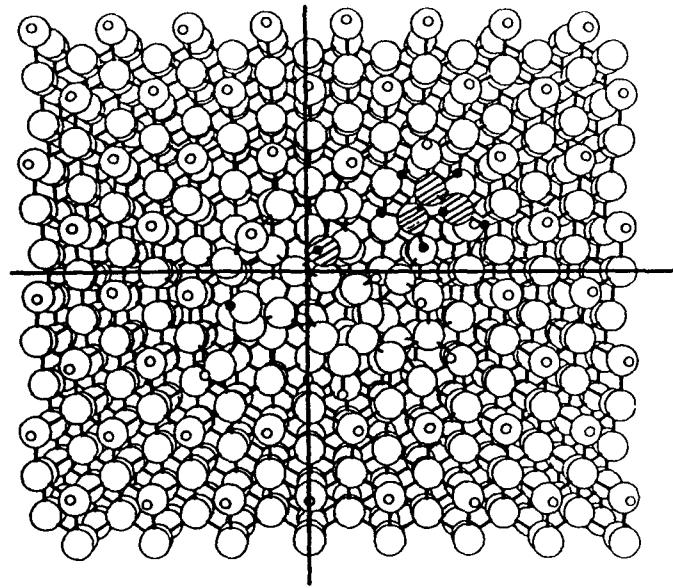
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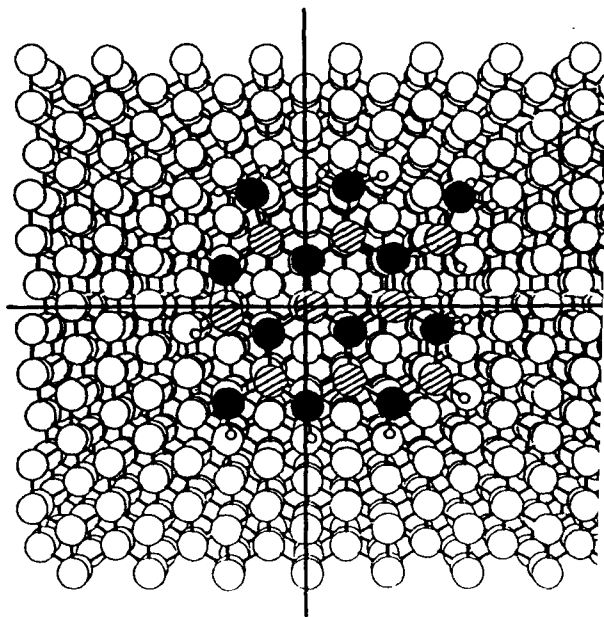
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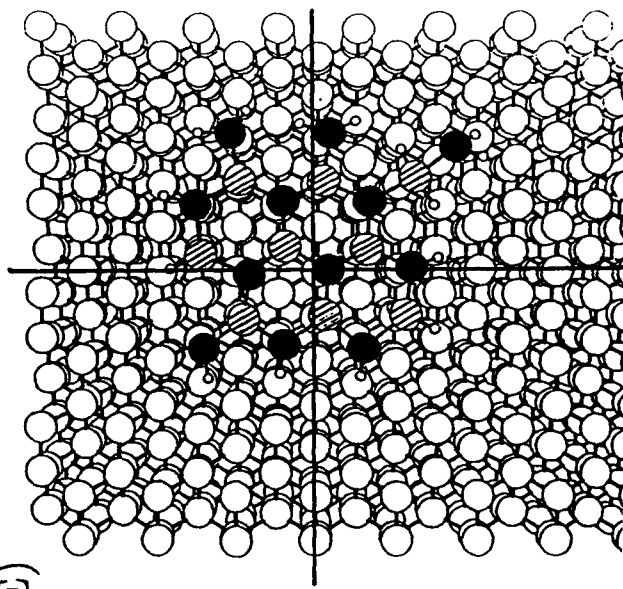
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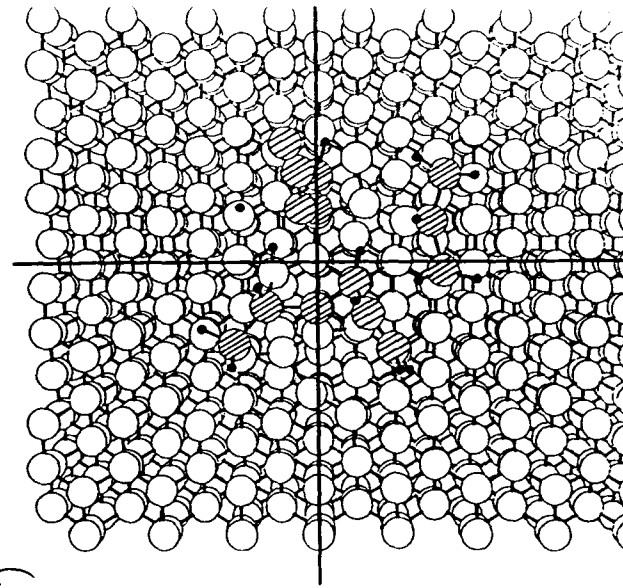
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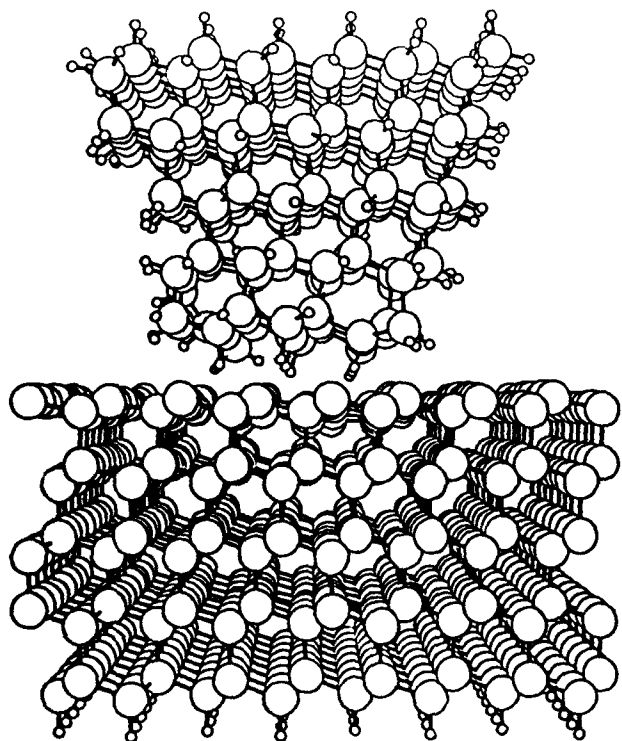
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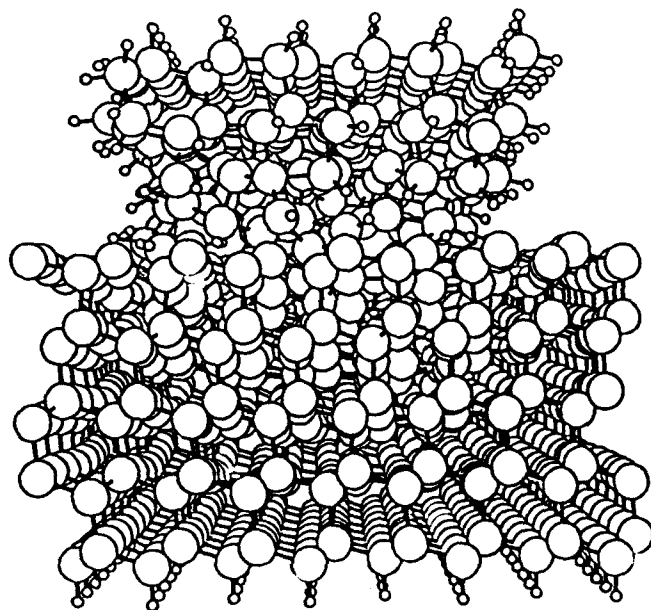
F)



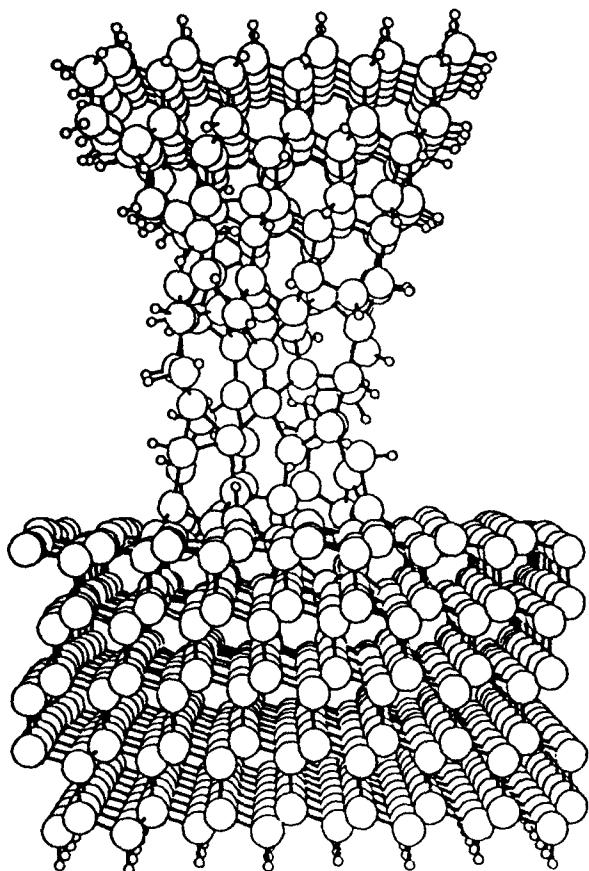
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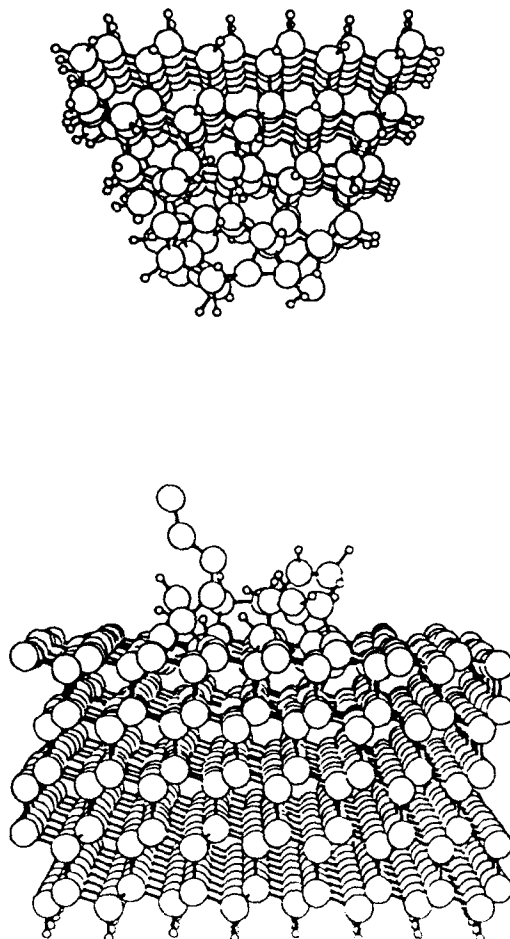
B)



C)



D)





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